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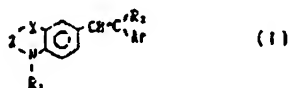
明 細 書

1. 発明の名称

感光体

2. 特許請求の範囲

1. 導電性支持体上に、下記一般式(1)で示されるスチリル化合物を含む感光層を有する感光体:



[式中、R₁は、それぞれ置換基を有してもよいアルキル基、アラルキル基、アリール基; R₂は水素原子、アルキル基、アラルキル基、または置換基を有してもよいアリール基; R₃はそれぞれ置換基を有してもよいアリール基、または置換基を有しない置換基; ZはXおよび置換原子と結合する基で置換基を有してもよい; R₁とR₂は一体となって環を形成してもよい]。

3. 発明の詳細な説明

産業上の利用分野

本発明は新規なスチリル化合物を含む感光層を有する感光体に関する。

従来の技術および課題

一般に電子写真においては、感光体の感光層表面に帯電、露光を行なって潜像形成を形成し、これを展像剤で展像し、可視化させ、その可視像をそのまま感光体上に露光させて複写像を得る直接方式、または感光体上の可視像を低感度の転写紙上に転写し、その転写像を定着させて複写像を得る間接転写方式あるいは感光体上の潜像形成を転写紙上に転写し、転写紙上の潜像形成を展像、定着する間接転写方式等が知られている。

この種の電子写真に使用される感光体の感光層を構成する材料として、従来のセレン、碲化カドミウム、有機感光材料の感光性材料が知られている。

これらの感光性材料は数多くの利点、例えば感光度電荷の伝達が少ないこと、あるいは光照射

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によって速やかに電荷を放電できることなどの利点を持っている反面、多量の欠点を持っている。例えば、セレン系感光体では、製造する条件が厳しく、製造コストが高く、また熱や機械的な衝撃に弱いため取り扱いに注意を要する。硫化カドミウム系感光体や酸化亜鉛感光体では、多量の環境下で安定した感光が得られない点や、増感剤として添加した色素がコロナ帯電による帯電劣化や露光による光退色を生じるため、長期間に渡って安定した特性を有することができないという欠点を有している。

一方、ポリビニルカルバゾールをはじめとする各種の有機光導電性ポリマーが提案されてきたが、これらのポリマーは、前述の無機系光導電材料に比べ、感度性、経年性などの点で優れているが、未だ充分な感度、耐久性及び環境変化による安定性の面で無機系光導電材料に劣っている。

また低分子量の有機光導電性化合物は、併用する結着材の種類、組成比率を選択することにより拡張の特性あるいは電子写真特性を制御すること

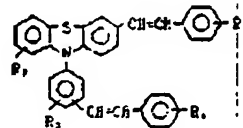
ができる点では好ましいものであるが、結着材と併用されるため、結着材に対する高い相溶性が要求される。

これらの低分子重および低分子量の有機光導電性化合物も結着材溶液中に分散させた感光体は、キャリアのトラップが多いため残留電位が大きく、感度が低い等の欠点を有する。そのために光導電性化合物に電荷輸送材料を配合して前記欠点を解決することが提案されている。

また、光導電性炭素の電荷発生機能と電荷輸送機能とをそれぞれ別個の物質に分担させるようにした機能分離型感光体が提案されている。このような機能分離型感光体において、電荷輸送層に使用される電荷輸送材料としては多くの有機化合物が挙げられているが実際には種々の問題点がある。例えば、米国特許3,189,447号公報に記載されている2,5-ビス(4-ジエチルアミノフェニル)-1,3,4-オキサジアゾールは、結着材に対する相溶性が低く、結晶が析出しやすい。米国特許3,820,989号公報に記載されている

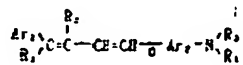
れている。

特開昭60-164752号公報には、下記一般式:



(式中、 $R_1 \sim R_2$ は上記公報中に記載のもの)で表わされるスチリル化合物が開示されている。

特開昭60-98437号公報には、下記一般式:



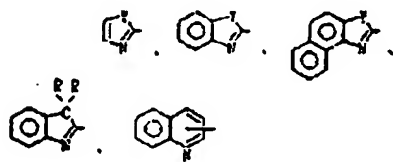
(式中、 $Ar_1 \sim Ar_2$ 、 $B_1 \sim B_2$ 、 n は上記公報中に記載のもの)で表わされるスチリル化合物が開示されている。

しかし、いずれの化合物も本発明の化合物と、その構造が異なる。

特開昭55-6424号公報には、下記一般式



(式中、 X 、 n 、 Ar は上記公報中に記載のもの)で表わされるスチリル化合物が開示され、 X として



(式中、 Y 、 R は上記公報中に記載のもの)が示さ

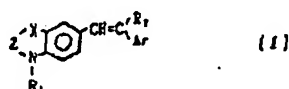
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発明が解決しようとする課題

本発明は以上の事実に基づいて成されたもので、起電材料に対する相溶性及び電荷輸送能に優れたスチリル化合物を光導電性物質として含有し、感度および電圧に優れ、繰り返し使用した場合の感度劣化が少なく、電子導電特性が安定している感電体を提供することを目的とする。

課題を解決するための手段

本発明は導電性支持体上に、下記一般式(1)で表されるスチリル化合物を含有する感光層を有する感光体：



[式中、R₁は、それぞれ置換基を有してもよいアルキル基、アラルキル基、アリール基；R₂は水素原子、アルキル基、アラルキル基、または置換基を有してもよいアリール基；Arはそれぞれ置換基を有してもよいアリール基、または複素環式基

環状基を成す。Arは、置換基、例えばアルキル基(メチル基あるいはエチル基等)、アルコキシ基(メトキシ基あるいはエトキシ基等)、アリール基(フェニル基等)、ヒドロキシ基、または置換アミノ基(ジエチルアミノ基、ジフェニルアミノ基等)等を有していてもよい。

Arは、R₁と重複し、または炭素原子あるいは酸素原子等を介して結合し、ArおよびR₂が結合している炭素原子とともに環を形成してもよい。

Xは酸素原子、イオウ原子または窒素原子を成す。Xが窒素原子であるとき、置換基、例えばR₁と同様のものを有していてもよい。

Zは、XおよびR₁が結合している空価と結合する基、例えば-C(H)-、-C(H)₂-、-C(H)=C(H)-あるいは-C(H)-等を成す。Zは置換基、例えば、アルキル基(メチル基あるいはエチル基等)、アリール基(例えばフェニル基等)を有していてもよい。

本発明の一般式(1)で表されるスチリル化合物の好ましい具体例としては例えば次の構造式を有

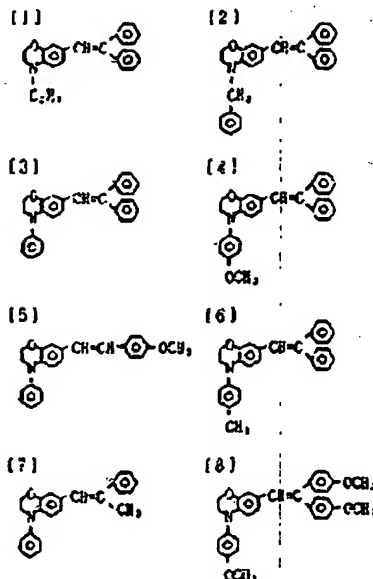
するXは酸素原子、イオウ原子、または置換基を有してもよい窒素原子；ZはXおよび窒素原子と結合する炭素で置換基を有してもよい；R₂とArは一体となって環を形成してもよい)に関する。

一般式(1)中、R₁はアルキル基、例えばメチル基あるいはエチル基等、アラルキル基、例えばベンジル基あるいはフェニル基等、またはアリール基、例えばフェニル基等を成す。それらの基は、置換基、例えばメチル基あるいはエチル基等のアルキル基またはメトキシ基あるいはエトキシ基等のアルコキシ基を有していてもよい。

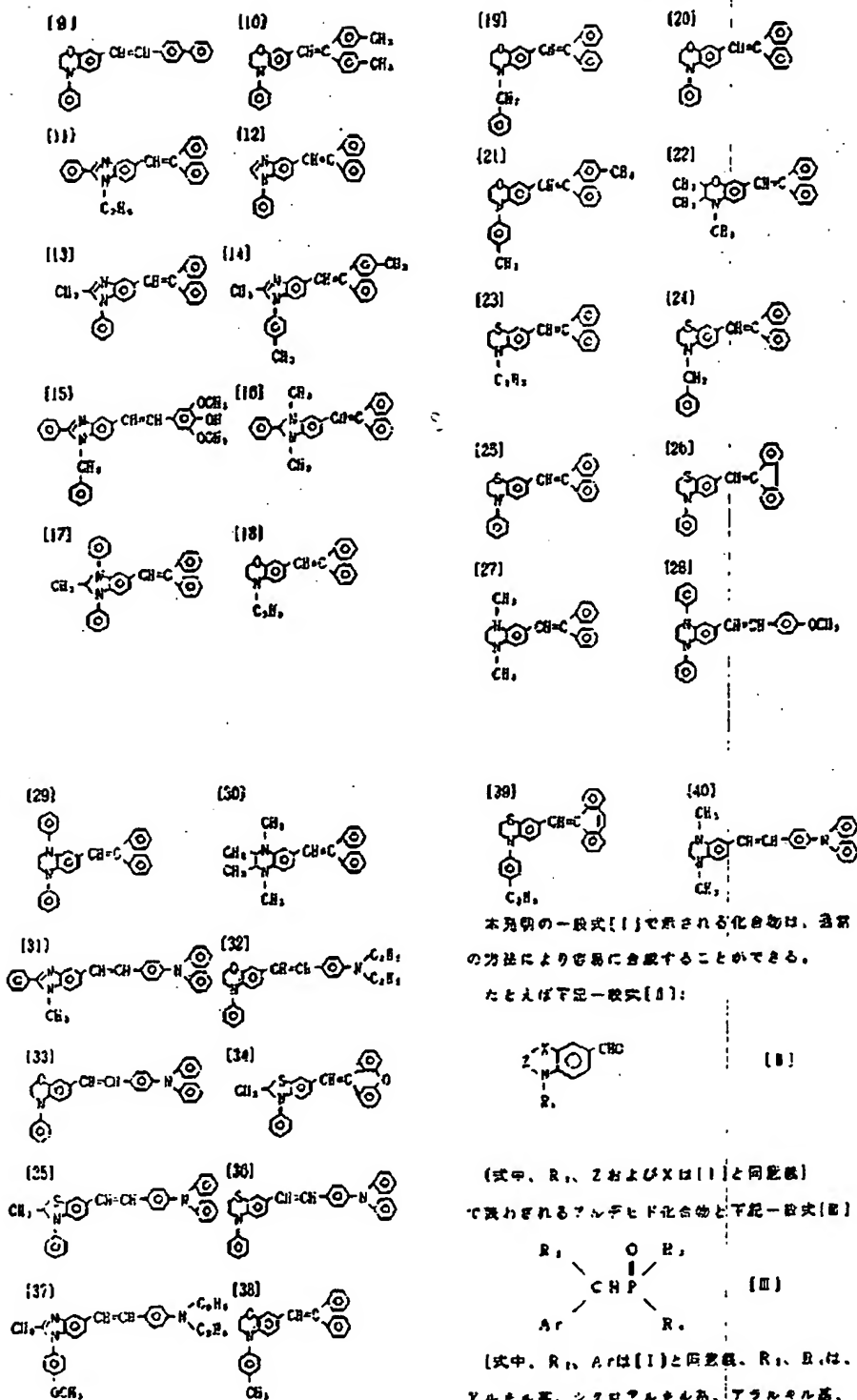
R₂は水素原子、アルキル基、例えばメチル基あるいはエチル基等、アラルキル基、例えばベンジル基あるいはフェニル基等、アリール基、例えばフェニル基等を成す。R₂がアリール基であるとき、置換基、例えばメチル基、エチル基等のアルキル基あるいはメトキシ基、エトキシ基等のアルコキシ基等を有していてもよい。

Arは、アリール基、例えばフェニル基等、環

するものがあげられるが、これらに限定されるものではない。



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により合成することができる。

一般式(II)で表わされるリン化合物のR₁、R₂は、特にシクロヘキシル基、ベンジル基、フェニル基、アルキル基が好ましい。

上記方法における反応剤としては、例えば炭化水素、アルコール類、エーテル類が良好で、メタノール、エタノール、イソプロパノール、ブタノール、2-メトキシエタノール、1,2-ジメトキシエタン、ビス(2-メトキシエチル)エーテル、ジオキサン、テトラヒドロフラン、トリエン、キシレン、ジメチルスルホキシド、N,N-ジメチルホルムアミド、N-メチルピロリドン、1,3-ジメチル-2-イミダゾリジノンなどが挙げられる。中でも極性溶媒、例えばN,N-ジメチルホルムアミド及びジメチルスルホキシドが好適である。

溶剤としては苛性ソーダ、苛性カリ、ナトリウムアミド、氷炭ナトリウム及びナトリウムメタラート、ナトリウムエテラート、カリウムメタラート、カリウムエテラート、カリウム-*tre*-ブ

たとえば、支持体上に電荷発生材料と、ステリル化合物を樹脂バインダーに分散させて成る感光層を付けた基層感光体や、支持体上に電荷発生材料を主成分とする電荷発生層を設け、その上に電荷輸送層を設けた所謂積層感光体等がある。本発明のステリル化合物は光導電性物質であるが、電荷輸送材料として作用し、光を吸収することにより発生した電荷担体を、極めて効率よく輸送することができる。

基層型感光体を作製するためには、電荷発生材料の微粒子を樹脂溶媒もしくは、電荷輸送材料と樹脂を溶媒した溶媒中に分散せしめ、これを導電性支持体上に塗布乾燥すればよい。この時の感光層の厚さは3~30μm、好ましくは5~20μmがよい。使用する電荷発生材料の量が少な過ぎると感度が悪く、多過ぎると耐電性が悪くなったり、感光層の機械的強度が弱くなったりし、感光層中に占める割合は樹脂1重量部に対して0.01~3重量部、好ましくは0.2~2重量部の範囲がよい。

トキシド、α-ブチルリチウムなどのアルコラートが用いられる。

反応温度は約0℃~約100℃まで広範囲に選択することが出来る。好ましくは10℃~約80℃である。

また、本発明によって使用される化合物(II)はリン化合物のみわけて対応する第4級ホスホニウム塩、例えばトリフェニルホスホニウム塩を使用し、ウィッティヒ(Wittig)の方法によりホスホリレンの段階を経て、アルデヒド化合物(III)と反応することによりステリル化合物(I)を合成してもよい。

本発明の感光体は前記一般式(I)で示されるステリル化合物を1種または2種以上含有する感光層を有する。また、他の電荷輸送材料、例えばヒドラゾン化合物や他のステリル化合物と組み合わせることによっても良好な電子伝導特性を得ることができる。

各種の形態の感光体は知られているが、本発明の感光体はそのいずれの感光体であってもよい。

積層型感光体を作製するには、導電性支持体上に電荷発生材料を真空蒸着するか、あるいは、アミン等の溶媒に溶解せしめて塗布するか、原料を適当な溶媒もしくは必要があればバインダー樹脂中を溶解させた溶媒中に分散させて分散した塗布液を塗布乾燥した後、その上に電荷輸送材料およびバインダーを含む樹脂を塗布乾燥して得られる。

真空蒸着する場合、たとえば亜金属フタロンアニン、チタニルフタロンアニン、アルミクロロフタロンアニンなどのフタロニアニン類が用いられる。また、分散させる場合は、たとえばビスアゾ染料などが用いられる。

このときの電荷発生層の厚みは4μm以下、好ましくは2μm以下がよく、電荷輸送層の厚みは3~30μm、好ましくは5~20μmがよい。

電荷輸送層中の電荷輸送材料の割合はバインダー樹脂1重量部に対して0.2~2重量部、好ましくは、0.3~1.3重量部である。

本発明の感光体はバインダー樹脂とともに、ハロゲン化パラフィン、ポリ塩化ビフェニル、ジメ

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テルナフタレン、ジブチルアクリレート、 α -ターフェニルなどの可塑剤やタロラニル、テトラシアノエチレン、2,4,7-トリニトロフルオレン、5,6-ジシアノベンジキノン、テトラシアノキノジメタン、テトラフルフルフルフル酸、3,5-ジニトロ安息香酸等の電子吸引性増感剤、ノバルバイオレット、ローダミンB、シアニン染料、ビリリウム塩、チアビリリウム塩等の増感剤を使用してもよい。

また、酸化防止剤や紫外線吸収剤、分散助剤、抗腐蝕剤等も適宜使用してもよい。

本発明において使用される電気伝導性のバインダー樹脂としては、電気伝導性であるそれ自体公知の熱可塑性樹脂あるいは熱硬化性樹脂、光硬化性樹脂や光導電性樹脂等の結着剤を使用できる。

適当な導電性樹脂の例は、これに限定されるものではないが、飽和ポリエステル樹脂、ポリアミド樹脂、アクリル樹脂、ニチレン-酢酸ビニル樹脂、イオン交換オレフィン共重合体(アイオノマー)、スチレン-ブタジエンブロック共重合体、

ール系樹脂、インダスロン系樹脂、スタアリウム系樹脂、アズレン系樹脂、フタロシアニン系樹脂等の有機物質や、セレン、セレン・テルル、セレン・碲素などのセレン合金、酸化カドミウム、セレン化カドミウム、酸化亜鉛、アモルファスシリコン等の無機物質が挙げられる。これ以外でも、光を吸収し極めて高い電圧で電荷発射を発生する材料であれば、いずれの材料であっても使用することができる。

本発明の感光体に用いられる導電性支持体としては、銅、アルミニウム、銀、鉄、亜鉛、ニッケル等の金属や合金の箔ないしは板をシート状又はドラム状にしたものが使用され、あるいはこれらの金属を、プラスチックフィルム等に蒸着、無電解メッキしたもの、あるいは導電性ポリマー、酸化インジウム、酸化スズ等の導電性化合物の層を同じく蒸着あるいはプラスチックフィルムなどの支持体上に塗布もしくは成膜によって設けられたものが用いられる。

本発明のスタリル化合物を用いた感光体の構成

ポリカーボネート、塩化ビニル-酢酸ビニル共重合体、セルロースエステル、ポリイミド、ステロール樹脂等の熱可塑性樹脂；エポキシ樹脂、ウレタン樹脂、シリコン樹脂、フェノール樹脂、メタクリン樹脂、キレテン樹脂、アルキッド樹脂、熱硬化アクリル樹脂等の熱硬化性樹脂；光硬化性樹脂；ポリビニルカルバゾール、ポリビニルピレン、ポリビニルアントラセン、ポリビニルピロール等の光導電性樹脂である。

これらは単独で、または組合せて使用することができる。

これらの電気伝導性樹脂は必ずしも完全に $1 \times 10^{12} \Omega \cdot \text{cm}$ 以上の体積抵抗を有することが望ましい。

電荷発生材料としては、ビスアゾ系染料、トリアリールメタン系染料、チアジン系染料、オキサジン系染料、キサンテン系染料、シアニン系染料、スタリル系染料、ビリリウム系染料、アゾ系染料、キナクリドン系染料、インジゴ系染料、ペリレン系染料、多環キノロン系染料、ビスベンズイミダゾ

例を第1図から第5図に模式的に示す。

第1図は、基板(1)上に光導電性材料(3)と電荷輸送材料(2)を結着剤に配合した感光層(4)が形成された感光体であり、電荷輸送材料として本発明のスタリル化合物が用いられている。

第2図は、感光層として電荷発生層(6)と、電荷輸送層(5)を有する積層分離型感光体であり、電荷発生層(6)の裏面に電荷輸送層(5)が形成されている。

電荷輸送層(5)中に本発明のスタリル化合物が配合されている。

第3図は、第2図と同様に電荷発生層(6)と、電荷輸送層(5)を有する積層分離型感光体であるが、第2図とは逆に電荷輸送層(5)の表面に電荷発生層(6)が形成されている。

第4図は、第1図の感光体の裏面にさらに保護層(7)を設けたものであり、感光層(4)は電荷発生層(6)と、電荷輸送層(5)を有する積層分離型感光体であってもよい。

第5図は、基板(1)と感光層(4)の間に中間層

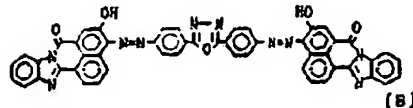
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し実施例1で用いたスチリル化合物(3)の代りにスチリル化合物(4)、(5)、(7)の各々を用いる感光体を作製した。

こうして得られた感光体について、実施例1と同様の方法で V_{90} 、 $E_{1/2}$ 、DDRを測定した。

実施例5

下記一般式(B)で表されるビスアゾ化合物



0.45部、ポリスチレン樹脂(分子量40000)

0.45部をシクロヘキサン50部とともにサンドグライNDERにより分散させた。得られたビスアゾ化合物の分散液を厚さ100 μ mのアルミ化マイラー上にフィルムアプリーケーターを用いて、乾燥膜厚が0.3 μ mとなる様に塗布した後乾燥させた。このようにして得られた電荷発生層の上にスチリル化合物(10)70部およびポリアリレート樹脂(U-100;ユニチカ社製)70部を、

せた。

得られた多環キノン系原料の分散液を厚さ100 μ mのアルミ化マイラー上にフィルムアプリーケーターを用いて、乾燥膜厚が0.4 μ mとなる様に塗布した後乾燥させた。このようにして得られた電荷発生層の上にスチリル化合物(20)60部およびポリアリレート樹脂(U-100;ユニチカ社製)50部を、1,4-ジオキサン600部に溶解した溶液を乾燥膜厚が18 μ mになるように塗布し、乾燥させて電荷移送層を形成した。

このようにして、2層からなる感光層を有する電子写真感光体を作製した。こうして得られた感光体について実施例1と同様の方法で V_{90} 、 $E_{1/2}$ 、DDRを測定した。

実施例10~11

実施例9と同様の方法で同一の構成のもの、但し実施例9で用いたスチリル化合物(20)の代りにスチリル化合物(21)、(25)を各々を用いる感光体を作製した。

こうして得られた感光体について、実施例1と

1,4-ジオキサン400部に溶解した溶液を乾燥膜厚が16 μ mになるように塗布し、電荷移送層を形成した。この様に、2層からなる感光層を有する電子写真感光体を作製した。

実施例6~8

実施例5と同様の方法で同一の構成のもの、但し実施例5で用いたスチリル化合物(10)の代りにスチリル化合物(11)、(12)、(13)を各々を用いる感光体を作製した。

こうして得られた感光体について、実施例1と同様の方法で V_{90} 、 $E_{1/2}$ 、DDRを測定した。

実施例9

下記一般式(C)で表される多環キノン系原料

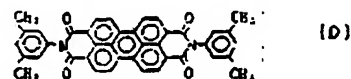


0.45部、ポリカーボネート樹脂(バンライトB-13000;帝人化成社製)0.45部をジクロルエタン50部とともにサンドミルにより分散さ

同様の方法で V_{90} 、 $E_{1/2}$ 、DDRを測定した。

実施例12

下記一般式(D)で表されるペリレン系原料



0.45部、フタラール樹脂(BX-1;清水化学工業社製)0.45部をジクロルエタン50部とともにサンドミルにより分散させた。

得られたペリレン系原料の分散液を厚さ100 μ mのアルミ化マイラー上にフィルムアプリーケーターを用いて、乾燥膜厚が0.4 μ mとなる様に塗布した後乾燥させた。このようにして得られた電荷発生層の上にスチリル化合物(26)50部およびポリカーボネート樹脂(PC-2;三菱化学社製)50部を、1,4-ジオキサン400部に溶解した溶液を乾燥膜厚が18 μ mになるように塗布し、電荷移送層を形成した。

このようにして、2層からなる感光層を有する

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電子写真感光体を作製した。こうして得られた感光体について実施例 1 と同様の方法で V_0 、 $E_{1/2}$ 、DDR を測定した。

実施例 3 ~ 4

実施例 1 2 と同様の方法で同一の構成のもの、但し実施例 1 2 で用いたスチリル化合物 [20] の代りにスチリル化合物 [24]、[28] を各々用いる感光体を作製した。

こうして得られた感光体について、実施例 1 と同様の方法で V_0 、 $E_{1/2}$ 、DDR を測定した。

実施例 5

チタニウムクロロアニン 0.45 部、ブタロール樹脂 (B-Mer: 日本化学工業社製) 0.45 部をジクロルエタン 50 部とともにアソニルにより分散させた。

得られたクロロアニン顔料の分散物を厚さ 100 μm のアルミ化ワイヤー上にフィルムアプリアーターを用いて、乾燥膜厚が 0.3 μm となる様に塗布した後乾燥させた。このようにして得られた電荷発生層の上にスチリル化合物 [7] 50 部

を塗布し、減圧下 120°C で乾燥した。

こうして得られた光導電性組成物 10 部を乾燥硬化化アクリル樹脂 (アクリリック A 405: 大日本インキ社製) 22.5 部、メラミン樹脂 (スーパーヘンカミン 1820: 大日本インキ社製) 7.5 部、同定したスチリル化合物 [3] 1.5 部を、メチルエチルケトンとキシレンを同量に混合した混合溶剤 100 部とともにボールミルボットに入れて 45 時間分散して感光性塗液を調製し、この塗液をアルミニウム基体上に塗布、乾燥して厚さ約 15 μm の感光層を形成させ感光体を作製した。

こうして得られた感光体について、実施例 1 と同様の方法、但しコロナ電圧を +6 Kv で行なって V_0 、 $E_{1/2}$ 、DDR を測定した。

実施例 9 ~ 21

実施例 1 8 と同様の方法で同一の構成のもの、但し実施例 1 8 で用いたスチリル化合物 [3] の代りにスチリル化合物 [20]、[33]、[38] を各々用いる感光体を作製した。

こうして得られた感光体について、実施例 1 8

およびポリカーボネート樹脂 (PC-Z: 三井化学社製) 50 部を 1,4-ジオキサン 400 部に溶解した溶液を乾燥膜厚が 18 μm になるように塗布し、電荷発生層を形成した。

このようにして、2 層からなる感光層を有する電子写真感光体を作製し、実施例 1 と同様の方法で V_0 、 $E_{1/2}$ 、DDR を測定した。

実施例 16 ~ 17

実施例 1 5 と同様の方法で同一の構成のもの、但し実施例 1 5 で用いたスチリル化合物 [7] の代りにスチリル化合物 [13]、[18] を各々用いる感光体を作製した。

こうして得られた感光体について、実施例 1 と同様の方法で V_0 、 $E_{1/2}$ 、DDR を測定した。

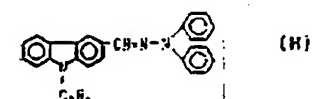
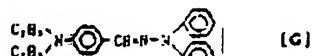
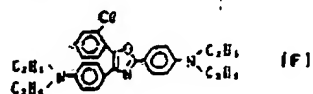
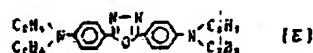
実施例 8

銅クロロアニン 50 部とナトリウム銅フタロシアニン 0.2 部を 98% 濃硫酸 500 部に充分攪拌しながら溶解させ、これを水 5000 部にあげ、銅クロロアニンとナトリウム銅フタロシアニンの光導電性材料組成物を析出させた後、

と同様の方法で V_0 、 $E_{1/2}$ 、DDR を測定した。

比較例 1 ~ 4

実施例 1 8 と同様の方法で同一の構成のもの、但し実施例 1 8 で用いたスチリル化合物の代りに下記化合物 [E]、[F]、[G]、[H] を各々用いる以外は実施例 1 8 と全く同様にして感光体を作製した。

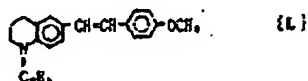
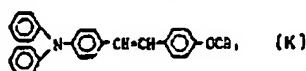
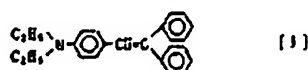
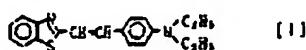


こうして得られた感光体について、実施例 1 8 と同様の方法で V_0 、 $E_{1/2}$ 、DDR を測定した。

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比較例 5～8

実施例 18 と同様の方法で同一の誘導体のもの、
但し実施例 18 で用いたステリル化合物 (5) の代
りに下記ステリル化合物 (I)、(J)、(K)、(L)
を各々用いる以外は実施例 18 と全く同様にして
感光体を作製した。



こうして得られた感光体について、実施例 18
と同様の方法で V_{90} 、 $E_{1/2}$ 、DDR を測定した。

実施例 1～21、比較例 1～8 で得られた感光
体の V_{90} 、 $E_{1/2}$ 、DDR の測定結果を表 1 に示

表 1

	V_{90} (V)	$E_{1/2}$ (lux·sec)	DDR (%)
実施例 1	-660	1.2	2.7
実施例 2	-650	6.5	3.1
実施例 3	-660	0.7	2.8
実施例 4	-660	0.7	2.6
実施例 5	-650	1.0	3.5
実施例 6	-660	0.6	2.8
実施例 7	-650	0.8	3.2
実施例 8	-660	1.0	2.7
実施例 9	-670	1.2	2.3
実施例 10	-660	1.3	2.6
実施例 11	-670	1.0	2.4
実施例 12	-650	1.3	2.8
実施例 13	-670	1.8	2.3
実施例 14	-670	1.5	2.4
実施例 15	-660	0.7	2.7
実施例 16	-650	0.6	3.1

とを示す。

表 1 からわかるように、本発明の感光体は積層
型でも単層型でも電荷保持性が充分あり、暗保
率も感光体としては充分使用可能な程度に小さく、
また、感度においても優れていることがデータよ
り明らかである。

更に、市販の電子写真感光体 (キノルタカメラ
社製:EP-350Z) による正電荷時の繰り返し
実写テストを実施例 18 の感光体において行なっ
たが、1000 枚のコピーを行なっても、初期、
最終面像において解像性が優れ、感度変化が無く、
鮮明な面像が得られ、本発明の感光体は繰り返し
特性も安定していることがわかる。

(以下、省略)

表 1 (続表)

	V_{90} (V)	$E_{1/2}$ (lux·sec)	DDR (%)
実施例 17	-660	0.6	2.8
実施例 18	+620	0.9	13.0
実施例 19	+610	0.8	13.7
実施例 20	+610	1.0	14.1
実施例 21	+620	0.7	13.1
比較例 1	+620	36.0	6.5
比較例 2	+600	5.7	14.0
比較例 3	+600	3.2	14.3
比較例 4	+610	4.7	13.2
比較例 5	+620	15.0	12.0
比較例 6	+610	5.8	11.6
比較例 7	+600	6.5	13.7
比較例 8	+620	8.3	12.2

発明の効果

本発明は感光体に有用な光導電性化合物を提供
した。

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本発明の光導電性化合物はスチリル化合物であり、特に電荷輸送材料として有用である。

本発明のスチリル化合物を有する感光体は、感度、電荷輸送性、初期表面電位、暗減衰率等の感光体特性に優れ、繰り返し使用に対する疲労度も少ない。

4. 図面の簡単な説明

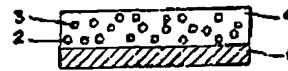
第1図～第5図は本発明に係る感光体の模式図であって、第1図、第4図、第5図は導電性支持体上に感光層を積層してなる分散型感光体の構造を示し、第2図、第3図は導電性支持体上に電荷発生層と電荷輸送層を積層してなる層型分散型感光体の構造を示す。

- | | |
|----------|----------|
| 1…導電性支持体 | 2…電荷輸送材料 |
| 3…光導電性材料 | 4…感光層 |
| 5…電荷輸送層 | 6…電荷発生層 |
| 7…表面保護層 | 8…中間層 |

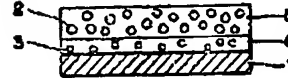
特許出願人 インテルカメラ株式会社

代理人 弁護士 青山 誠 ほか1名

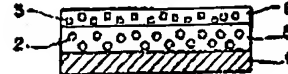
第1図



第2図



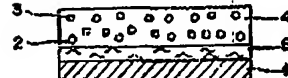
第3図



第4図



第5図



Japanese Kokai Patent Application No. Hei 4[1992]-46352 A

Job No.: 166-101327

Translated from Japanese by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

Ref.: JP04046352A

JAPANESE PATENT OFFICE
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KOKAI PATENT APPLICATION NO. HEI 4[1992]-46352

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Examination Request: Not filed

PHOTOSENSITIVE MATERIAL

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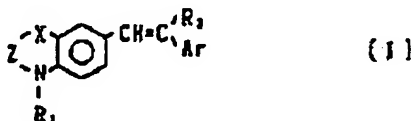
Agents:

Tamotsu Aoyama, patent attorney,
and 1 other

[There are no amendments to this patent.]

Claim

A type of photosensitive material characterized by the fact that it has a photosensitive layer containing a styryl compound represented by following formula (I) formed on an electroconductive substrate:



(where, R₁ represents an optionally substituted alkyl group, aralkyl group, or aryl group; R₂ represents a hydrogen atom, alkyl group, aralkyl group, or optionally substituted aryl group; Ar represents an optionally substituted aryl group or heterocyclic group; X represents an oxygen atom, sulfur atom, or optionally substituted nitrogen atom; Z and X represent optionally substituted residual groups bonded with the nitrogen atom; R₂ and Ar may be bonded to each other to form a ring.)

Detailed explanation of the invention

Industrial application field

The present invention pertains to a novel type of photosensitive material containing a styryl compound.

Prior art and problems to be solved

Conventional electrophotography is made up of the following formats: in one format known as the direct system, the photosensitive layer of a photosensitive material is charged and exposed to form an electrostatic latent image, and the latent image is developed with a developing agent to form a visible image, which is directly fixed on the photosensitive material to obtain a visible picture. In another format known as the powder image transfer system, the visible image on the photosensitive material is transferred to a paper sheet or other transfer material, and the transferred image is then fixed to form a transferred picture. In yet another format known as the electrostatic transfer system, the electrostatic latent image on the photosensitive material is transferred to a transfer paper, and the electrostatic latent image on the transfer paper is developed and fixed.

Examples of materials for forming the photosensitive layer of the photosensitive material used in said electrophotographic method include selenium, cadmium sulfide, zinc oxide, and other inorganic photoconductive materials.

These photoconductive materials have many advantages, such as little dissipation of charge in the dark, and the ability of quickly dissipating the charge under light irradiation. On the other hand, it has various disadvantages. For example, for selenium based photosensitive materials, their manufacturing conditions are difficult to meet, their manufacturing costs are high, and, because they are weak under heat or mechanical impact, caution must be taken in their handling. On the other hand, for cadmium sulfide-based photosensitive material and the zinc oxide-based photosensitive materials, a stable sensitivity cannot be obtained in a humid environment, and the dye added as a sensitizing agent leads to corona discharge so that the charging property degrades and the light fading phenomenon is exhibited due to exposure. Consequently, it is impossible to have stable characteristics over a long time, which is undesired.

On the other hand, various organic photoconductive polymers, such as polyvinylcarbazole, etc., have been proposed. However, although these polymers are better than the above inorganic photoconductive materials with respect to film forming property and light weight, they are poorer than the inorganic photoconductive materials with respect to sensitivity, durability and stability against environmental variation.

Also, although low molecular weight organic photoconductive compounds have the advantage that the properties of the coating film or the electrophotographic characteristics can be controlled by selecting the type and proportion of binder, they must have good miscibility with the binder.

For the photosensitive material prepared by dispersing a high-molecular weight or low-molecular weight organic photoconductive compound in the binder resin, because there are a large number of carrier traps, the residual potential is high, and the sensitivity decreases. These are disadvantages. Consequently, the addition of a charge-transporting substance to the photoconductive compound has been proposed to solve the aforementioned problem.

Also, a function-separation type photosensitive material in which the charge-generation function and charge-transport function are performed by different substances has been proposed. For the function-separation type photosensitive material, many types of organic compounds have been proposed as the charge-transporting substance for use in the charge transport layer.

However, they have various problems. For example,

2,5-bis(p-diethylaminophenyl)-1,3,4-oxathiazole described in US Patent No. 3,189,447 has a poor miscibility with the binder, and the crystals tend to become exhausted. On the other hand, for the diarylalkane derivative described in US Patent No. 3,820,989, although the miscibility with the binder is good, when it is used repeatedly, the sensitivity varies. Also, for the melamine

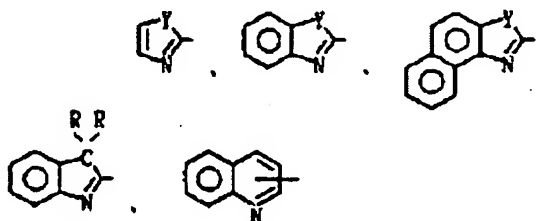
compound described in Japanese Kokai Patent Application No. Sho 54[1979]-59143, although it has a relatively good residual charge property, it nevertheless has a poor charging property and poor repeated operation characteristics. At present, there are few organic compounds having low molecular weight and excellent characteristics preferred for practical application in preparing photosensitive materials.

Japanese Kokai Patent Application No. Sho 55[1980]-6424 described a type of styryl compound represented by the following formula



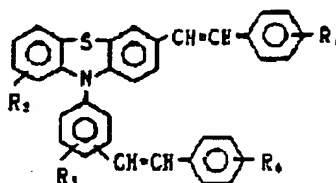
(where, X, n, Ar are defined in said patent application).

X represents



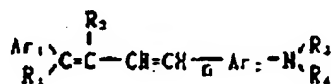
(where, Y and R are defined in said patent application).

Japanese Kokai Patent Application No. Sho 60[1985]-164752 described a type of styryl compound represented by the following formula:



(where, R₁-R₄ is defined in said patent application).

Japanese Kokai Patent Application No. Sho 60[1985]-98437 described a type of styryl compound represented by the following formula:



(where, Ar₁-Ar₂, R₁-R₄ are defined in said patent application).

However, all of these compounds are different in structure from the compounds of the present invention.

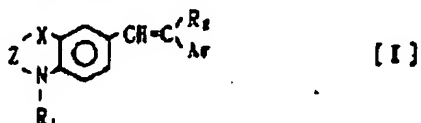
Problems to be solved by the present invention

The purpose of the present invention is to solve the problems of the prior art by providing a type of photosensitive material characterized by the fact that it is contained as a

photoconductive substance having excellent miscibility with the binder and an excellent charge-transport property, and it has excellent sensitivity and chargeability, little fatigue degradation in repeated use and a high stability of the electrophotographic characteristics.

Means to solve the problems

This invention provides a type of photosensitive material characterized by the fact that it has a photosensitive layer containing a styryl compound represented by following formula (I) formed on an electroconductive substrate:



(where, R_1 represents an optionally substituted alkyl group, aralkyl group, or aryl group; R_2 represents a hydrogen atom, alkyl group, aralkyl group, or optionally substituted aryl group; Ar represents an optionally substituted aryl group or heterocyclic group; X represents an oxygen atom, sulfur atom, or optionally substituted nitrogen atom; Z and X represent optionally substituted residual group bonded with the nitrogen atom; R_2 and Ar may be bonded to each other to form a ring).

In formula (I), R_1 represents an alkyl group such as methyl or ethyl, aralkyl groups such as benzyl or phenethyl, aryl group such as phenyl, etc. These groups may have substituents, such as a methyl group, ethyl group, or other alkyl group, or methoxy group, ethoxy group, or other alkoxy group.

R_2 represents a hydrogen atom, an alkyl group such as methyl or ethyl, aralkyl group such as benzyl or phenethyl, aryl group such as phenyl, etc. When R_2 represents an aryl group, it may have substituents, such as a methyl group, ethyl group, or other alkyl group, methoxy group, ethoxy group, or other alkoxy group, etc.

Ar represents an aryl group, such as phenyl, or a heterocyclic group. Ar may have substituents, such as an alkyl group (methyl group, ethyl group, etc.), alkoxy group (methoxy group, ethoxy group, etc.), aryl group (phenyl group, etc.), hydroxyl group, or substituted amino group (diethylamino group, diphenylamino group, etc.), etc.

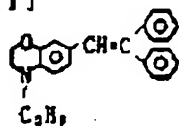
Ar may be bonded to R_2 either directly or via a carbon atom or oxygen atom, and Ar and R_2 can form a ring together with their carbon atoms.

X represents an oxygen atom, sulfur atom, or nitrogen atom. When X represents a nitrogen atom, it may have substituents, such as those listed for R_1 .

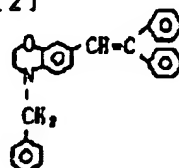
Z represents the residual group bonded to nitrogen that is bonded to X and R₁, such as -CH₂-, -CH₂CH₂-, -CH=, etc. Z may have substituents, such as an alkyl group (methyl group, ethyl group, etc.), aryl group (such as phenyl group, etc.).

The following are the structural formulas of the preferable examples of the styryl compounds represented by formula (I) in the present invention. However, they are not limited to what is listed here.

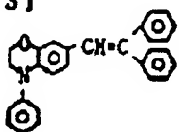
[1]



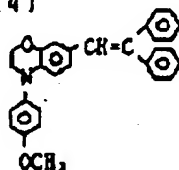
[2]



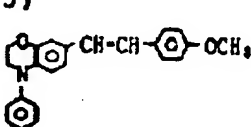
[3]



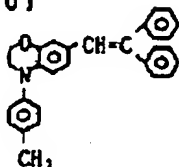
[4]



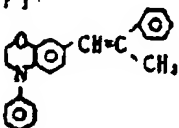
[5]



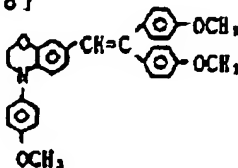
[6]

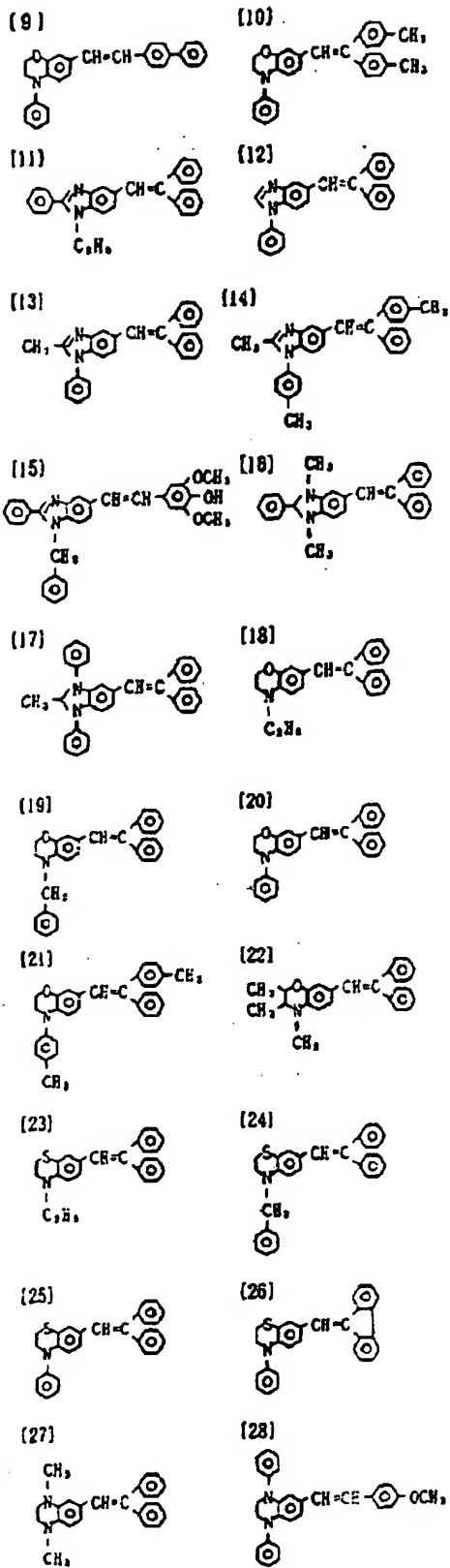


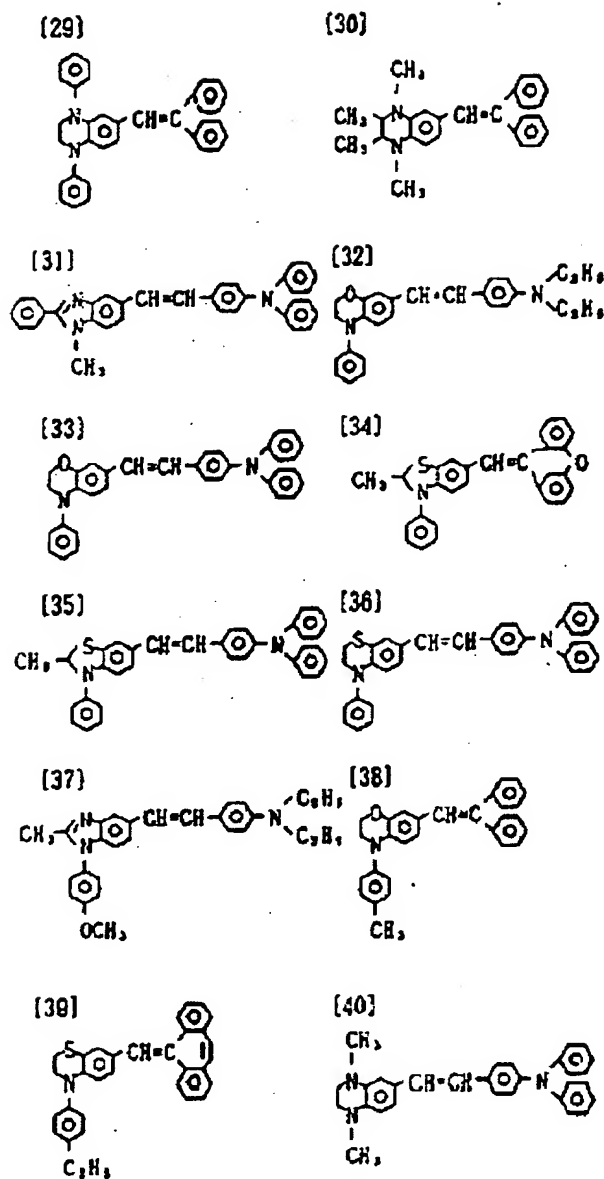
[7]



[8]

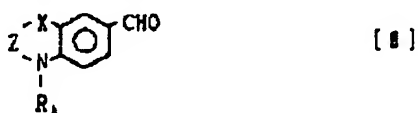




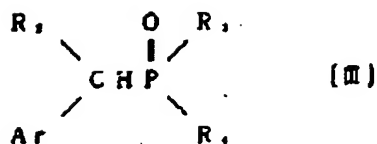


The compound represented by formula (I) of the present invention can be prepared easily using the conventional method.

For example, it may be prepared in a condensation reaction between an aldehyde compound represented by the following formula (II):



(where, R₁, Z and X have the same meanings as those in formula (I))
and a phosphorus compound represented by the following formula (III):



(where, R_2 and Ar have the same meanings as those in (I); R_3 and R_4 represent alkyl groups, cycloalkyl groups, aralkyl groups, or aryl groups).

The preferable groups of R_3 and R_4 in the phosphorus compound represented by formula (III) include cyclohexyl groups, benzyl groups, phenyl groups, and alkyl groups.

Examples of good solvents for performing the reaction in said method include hydrocarbons, ethers, alcohols, such as methanol, ethanol, isopropanol, butanol, 2-methoxy ethanol, 1,2-dimethoxyethane, bis(2-methoxyethyl) ether, dioxane, tetrahydrofuran, toluene, oxylene, dimethyl sulfoxide, N,N-dimethylformamide, N-methylpyrrolidone, 1,3-dimethyl-2-imidazolinone, etc. Among them, polar solvents such as N,N-dimethylformamide and dimethyl sulfoxide are preferred.

Examples of binders include caustic soda, caustic potassium, sodium amide, sodium hydride, sodium methylate, sodium ethylate, potassium methylate, potassium ethylate, potassium tert-butoxide, n-butyllithium, and other alcoholates.

The reaction temperature can be selected in a wide range of about 0°C to about 100°C, or preferably in the range of about 10°C to about 80°C.

Also, compound (III) used in the present invention may also be prepared by using a quaternary phosphonium salt instead of said phosphorus compound. For example, one may make use of a triphenyl phosphonium salt to condense with an aldehyde compound (II) through a phosphorylene step using the Wittig reaction to form styryl compound (I).

The photosensitive material of the present invention has a photosensitive layer containing one or several types of the styryl compound represented by formula (I). Also, by using it in combination with other charge-transporting substances, such as hydrazone compounds and other styryl compounds, it is possible to realize even better electrophotographic characteristics.

There are various forms of photosensitive materials. Any form may be adopted for the photosensitive material of the present invention. For example, it may be a single-layer photosensitive material prepared by forming a photosensitive layer having a charge-generating substance and said styryl compound dispersed in a resin binder on a substrate, and it may be a so-called laminated photosensitive material prepared by forming a charge generation layer mainly made of a charge-generating substance on a substrate and then forming a charge transport layer on said charge generation layer. The styryl compound of the present invention is a photoconductive substance. However, it functions as a charge-transporting substance. It transfers the charge carriers generated by absorbing light at very high efficiency.

When said single-layer photosensitive material is formed, the operation is as follows. Fine particles of the charge-generating substance are dispersed in a resin solution or a solution prepared by dissolving the charge-transporting substance and resin. It is then coated and dried on an electroconductive substrate. In this case, the photosensitive layer has a thickness of 3-30 μm , or preferably in the range of 5-20 μm . If the quantity of charge-generating substance is too small, the sensitivity is poor. On the other hand, if it is too large, the charging property degrades, the mechanical strength of the photosensitive layer decreases, and the mechanical strength of the photosensitive layer decreases. The proportion in the photosensitive layer with respect to 1 part by weight of the resin should be in the range of 0.01-3 parts by weight, or preferably in the range of 0.2-2 parts by weight.

When said laminated photosensitive material is prepared, the charge-generating substance is coated on the electroconductive substrate by means of vacuum vapor deposition or coating as an amine solution or the like. In another format, after coating and drying of a coating solution prepared by dissolving a pigment in an appropriate solvent and, as needed, a binder resin, a solution containing the charge-transporting substance and binder is coated and dried on it.

In the case of vacuum vapor deposition, for example, a nonmetallic phthalocyanine, titanyl phthalocyanine, aluminum chlorophthalocyanine, or other phthalocyanine compound is used. In the case of dispersion, for example, a bisazo pigment or the like may be used.

In this case, the thickness of the charge generation layer should be 4 μm or less, or preferably 2 μm or less, and the thickness of the charge transport layer should be in the range of 3-30 μm , or preferably in the range of 5-20 μm .

The proportion of charge-transporting substance in the charge transport layer with respect to 1 part by weight of the binder resin should be in the range of 0.2-2 parts by weight, or preferably in the range of 0.3-1.3 parts by weight.

Together with the binder resin, the photosensitive material of the present invention may also contain a halogenated paraffin, polybiphenyl chloride, dimethylnaphthalene, dibutyl phthalate, o-terphenyl, and other plasticizers, chloranil, tetracyanoethylene, 2,4,7-trinitrofluororenone, 5,6-dicyanobenzoquinone, tetraanthraquinomethane, tetrachlorophthalic anhydride, 3,5-dinitrobenzoic acid, and other electronegative sensitizers, methyl violet, Rhodamine B, cyanine dye, pyrylium salt, thiapyrylium salt, and other sensitizers.

Also, oxidation inhibitors, UV absorbents, dispersion aids, precipitation inhibitors, etc. may be selected appropriately for use.

Examples of the binder resins having electrically insulating property used in the present invention include well known thermoplastic resins and thermosetting resins photocuring resins, photoconductive resins, and other binder that are electrically insulating.

Examples of the appropriate binder resins include saturated polyester resins, polyamide resins, acrylic resins, ethylene-vinyl acetate resins, ion crosslinked olefin copolymers (ionomers), styrene-butadiene block copolymers, polycarbonates, vinyl chloride-vinyl acetate copolymers, cellulose esters, polyimides, styrol resins, and other thermoplastic resins; epoxy resins, urethane resins, silicone resins, phenolic resins, melamine resins, xylene resins, alkyd resins, thermosetting acrylic resins, and other thermosetting resins; photocuring resins; polyvinylcarbazole, polyvinylpyrene, polyvinylanthracene, polyvinylpyrrole, and other photoconductive resins. However, the present invention is not limited to them.

They may be used either alone or as a mixture of several types.

These electrically insulating resins preferably have a volumetric resistance of $1 \times 10^{12} \Omega \cdot \text{cm}$ measured for each resin alone.

Examples of the charge-generating substances include bisazo-based pigments, triaryl methane-based dyes, thiazine-based pigments, oxazine-based dyes, xanthine-based dyes, cyanine-based pigments, styryl-based pigments, pyridium-based dyes, azo-based pigments, quinacridone-based pigments, indigo-based pigments, perylene-based pigments, phthalocyanine quinine-based pigments, bisbenzimidazole-based pigments, indazolone-based pigments, squaric salt-based pigments, azulene-based pigments, phthalocyanine-based pigments, and other organic substances, selenium, selenium/tellurium, selenium/arsenic, and other selenium alloys, cadmium sulfide, cadmium selenide, zinc oxide, amorphous silicon, and other inorganic substances. In addition, any material that can highly efficiently absorb light to generate charge carriers may be used.

Examples of the electroconductive substrates that can be used as the photosensitive material of the present invention include sheet and drums made of foils or sheets of copper, aluminum, silver, iron, zinc, nickel, and other metals and alloys; plastic films, etc. coated with said metals by means of vacuum vapor deposition or electroless plating; paper, plastic film, etc. coated or vapor deposited with a layer of electroconductive polymer, indium oxide, tin oxide, or other electroconductive compound.

Examples of the constitution of the photosensitive material using the styryl compound of the present invention are shown schematically in Figures 1-5.

As shown in Figure 1, the photosensitive material is prepared by forming photosensitive layer (4) composed of photoconductive material (3) and charge-transporting substance (2) together with a binder on substrate (1). The styryl compound of the present invention is used as the charge-transporting substance.

The photosensitive material shown in Figure 2 is a function-separation type photosensitive material having charge generation layer (6) and charge transport layer (5) as the

photosensitive layers. Charge transport layer (5) is formed on the surface of charge generation layer (6).

The styryl compound of the present invention is contained in said charge transport layer (5).

The photosensitive material shown in Figure 3 is a function-separation type photosensitive material having the same charge generation layer (6) and charge transport layer (5) as in Figure 2. However, the configuration is the reverse of that shown in Figure 2, with charge generation layer (6) formed on the surface of charge transport layer (5).

In the photosensitive material shown in Figure 4, surface protective layer (7) is formed on the surface of the photosensitive material shown in Figure 1. Photosensitive layer (4) may also be a function-separated type photosensitive material having charge generation layer (6) and charge transport layer (5).

As shown in Figure 5, intermediate layer (8) is set between substrate (1) and photosensitive layer (4). It is possible to form intermediate layer (8) to improve various properties, such as adhesion, coating property, protection of the substrate, and the property of charge injection from the substrate to the photosensitive layer.

The intermediate layer may be made of polyimide, polyamide, nitrocellulose, polyvinylbutyral, polyvinyl alcohol, or other polymer as is. It may also be made of a dispersion of tin oxide, indium oxide, or other low-resistance compound, or a vapor deposited film of aluminum oxide, zinc oxide, silicon oxide, etc.

The thickness of the intermediate layer is preferably 1 μm or less.

The surface protective layer may be made of acrylic resin, polyaryl resin, polycarbonate resin, polyurethane resin, or other polymer as is. It may also be made of a dispersion of tin oxide, indium oxide, or other low-resistance compound.

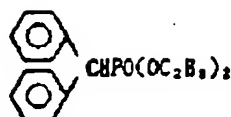
Also, it is possible to make use of an organic plasma film. As needed, the organic plasma polymer may contain oxygen, nitrogen, halogen, and atoms in Groups III and V of the Periodical Table appropriately.

The thickness of the surface protective layer is preferably 5 μm or less.

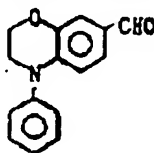
In the following, the present invention will be explained in more detail with reference to application examples. In the application examples, if not specified otherwise, "parts" refers to "parts by weight."

Synthesis example (Preparation of compound example (3))

3.04 g of the phosphate represented by the following formula



and 2.39 g of the aldehyde compound represented by the following formula



were dissolved in 30 mL of dimethylformamide. While it was cooled to 5°C or lower, a suspension prepared from 2 g of potassium tert-butoxide in 50 mL of dimethylformamide was added dropwise. Then, after the mixture was agitated at room temperature for 8 h, the mixture was allowed to stand overnight. The obtained mixture was added to 900 mL of ice water, followed by neutralization with dilute hydrochloric acid. After about 30 min, the deposited crystals were filtered out and washed with water. Then, they were recrystallized and refined by means of acetonitrile, forming 2.8 g of yellow acicular crystals.

(Yield is 72%)

The results of elemental analysis are listed below.

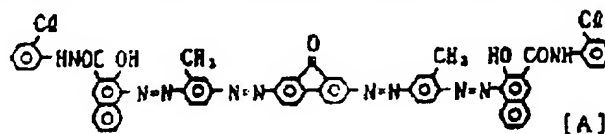
		C (%)	H (%)	N (%)
①	計算値 *	86.38	5.91	3.60
②	実験値	86.30	5.87	3.51

* C₂₁H₁₃N₃O

Key: 1 Computed data
2 Experimental data

Application Example 1

0.45 part of the bisazo compound represented by the following formula (A)



and 0.45 part of polyester resin (Pylon 200, product of Toyobo Co., Ltd.) were dispersed in 50 parts of cyclohexanone by means of a sand grinder. By means of a film applicator, the obtained dispersion of the bisazo compound was coated and dried on a 100-μm-thick aluminum-coated mylar film to form a layer with a dry thickness of 0.3 g/m². On this obtained charge generation

layer, a 16- μm -thick (dry film thickness) charge transport layer was formed by coating a solution prepared by dissolving 70 parts of styryl compound (3) and 70 parts of polycarbonate resin (K-1300, product of Teijin Ltd.) in 400 parts of 1,4-dioxane. In this way, an electrophotographic photosensitive material having a 2-layer photosensitive layer was obtained.

With a commercially available electrophotographic copier (EP-470Z, product of Minolta Camera Co., Ltd.), the following test was performed for the obtained photosensitive material. Corona charging was performed at -6 kV, the initial surface potential $V_0(\text{V})$, the exposure quantity $E_{1/2}(\text{lux} \cdot \text{sec})$ for reducing the potential to 1/2 the initial potential, and the dark decay rate $\text{DDR}_1(\%)$ with respect to the initial potential after allowing to stand in the dark for 1 sec were measured.

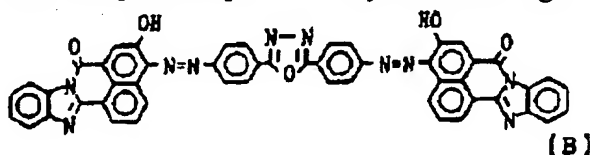
Application Examples 2-4

Also, using the same method and the same constitution as those in Application Example 1, photosensitive material samples were prepared except that styryl compounds (4), (5), (7) were used in place of said styryl compound (3) used in Application Example 1.

For the obtained photosensitive materials, the same method as that in Application Example 1 was adopted to measure the values of V_0 , $E_{1/2}$, and DDR_1 .

Application Example 5

0.45 part of the bisazo compound represented by the following formula (B)



and 0.45 part of polystyrene resin (molecular weight 40,000) were dispersed in 50 parts of cyclohexane by means of a sand grinder. The obtained dispersion of bisazo compound was coated with a film applicator and dried on a 100- μm -thick aluminum-coated mylar film to form a layer with a dry thickness of 0.3 g/m^2 . On this obtained charge generation layer, a 16- μm -thick (dry film thickness) charge transport layer was formed by coating a solution prepared by dissolving 70 parts of styryl compound (10) and 70 parts of polyacrylate resin (U-100, product of Unitika Ltd.) in 400 parts of 1,4-dioxane. In this way, an electrophotographic photosensitive material having a 2-layer photosensitive layer was obtained.

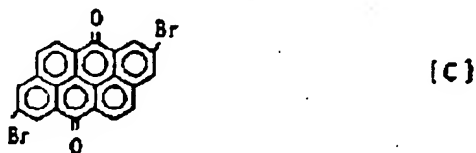
Application Examples 6-8

Photosensitive materials were prepared using the same method as that in Application Example 5, except that instead of styryl compound (10) used in Application Example 5, styryl compounds (11), (12) and (13) were used.

For the obtained photosensitive materials, the same method as that in Application Example 1 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Application Example 9

0.45 part of the polycyclic quinine-based pigment represented by the following formula (C)



and 0.45 part of polycarbonate resin (Panlite K-13000, product of Teijin Ltd.) were dispersed in 50 parts of dichloroethane by means of a sand grinder.

The obtained dispersion of the polycyclic quinine-based pigment was coated with a film applicator and dried on a 100- μ m-thick aluminum-coated mylar film to form a layer with a dry thickness of 0.4 g/m². On this obtained charge generation layer, a 18- μ m-thick (dry film thickness) charge transport layer was formed by coating a solution prepared by dissolving 60 parts of styryl compound (20) and 50 parts of polyacrylate resin (U-100, product of Unitika Ltd.) in 400 parts of 1,4-dioxane.

In this way, an electrophotographic photosensitive material having a 2-layer photosensitive layer was obtained. For the obtained photosensitive material, the same method as that in Application Example 1 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

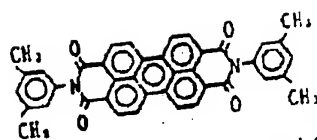
Application Examples 10-11

Photosensitive materials were prepared in the same structure and using the same method as that in Application Example 9, except that instead of styryl compound (20) used in Application Example 9, styryl compounds (21), (25) were used.

For the obtained photosensitive material, the same method as that in Application Example 1 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Application Example 12

0.45 part of a perylene-based pigment represented by the following formula (D)



[D]

and 0.45 part of butyral resin (BX-1, product of Sekisui Chemical Co., Ltd.) were dispersed in 50 parts of dichloroethane by means of a sand grinder.

The obtained dispersion of perylene-based pigment was coated with a film applicator and dried on a 100- μm -thick aluminum-coated mylar film to form a layer with a dry thickness of 0.4 g/m^2 . On this obtained charge generation layer, a 18- μm -thick (dry film thickness) charge transport layer was formed by coating a solution prepared by dissolving 50 parts of styryl compound (26) and 50 parts of polycarbonate resin (PC-2, product of Mitsubishi Gas Chemical Co., Ltd.) in 400 parts of 1,4-dioxane.

In this way, an electrophotographic photosensitive material having a 2-layer photosensitive layer was obtained. For the obtained photosensitive material, the same method as that in Application Example 1 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Application Examples 13-14

Photosensitive materials were prepared with the same structure and using the same method as that in Application Example 12, except that instead of styryl compound (26) used in Application Example 12, styryl compounds (24), (28) were used.

For the obtained photosensitive material, the same method as that in Application Example 1 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Application Example 15

0.45 part of titanil phthalocyanine and 0.45 part of butyral resin (BX-1, product of Sekisui Chemical Co., Ltd.) were dispersed in 50 parts of dichloroethane by means of a sand grinder.

The obtained dispersion of phthalocyanine was coated with a film applicator and dried on a 100- μm -thick aluminum-coated mylar film to form a layer with a dry thickness of 0.3 g/m^2 . On this obtained charge generation layer, a 18- μm -thick (dry film thickness) charge transport layer was formed by coating a solution prepared by dissolving 50 parts of styryl compound (7) and 50 parts of polycarbonate resin (PC-Z, product of Mitsubishi Gas Chemical Co., Ltd.) in 400 parts of 1,4-dioxane.

In this way, an electrophotographic photosensitive material having a 2-layer photosensitive layer was obtained. For the obtained photosensitive material, the same method as that in Application Example 1 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Application Examples 16-17

Photosensitive materials were prepared with the same structure and using the same method as that in Application Example 15, except that instead of styryl compound (7) used in Application Example 15, styryl compounds (13) and (18) were used.

For the obtained photosensitive material, the same method as that in Application Example 1 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Application Example 18

50 parts of copper phthalocyanine and 0.2 part of copper tetranitrophthalocyanine were dissolved in 500 parts of 98% concentrated sulfuric acid while being well agitated. The solution was poured into 5000 parts of water. After the photoconductive material composition of copper phthalocyanine and copper tetranitrophthalocyanine was dissipated, it was filtered out, water washed, and dried under reduced pressure at 120°C.

10 parts of the obtained photoconductive composition prepared above were mixed with 22.5 parts of thermosetting acrylic resin (Acrydick A 405, product of Dai-Nippon Ink Co., Ltd.), 7.5 parts of melamine resin (Superbeckamine J 820, product of Dai-Nippon Ink Co., Ltd.), and 15 parts of said styryl compound (3) together with 100 parts of a 1:1 mixture of methyl ethyl ketone and xylene as a mixed solvent, and the mixture was dispersed for 48 h to form a photosensitive solution. The solution was then coated on an aluminum substrate, and was dried to form a photosensitive material having a photosensitive layer with thickness of about 15 μm .

For the obtained photosensitive material, the same method as that in Application Example 1 (except that the corona charging was performed at +6 kV) was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

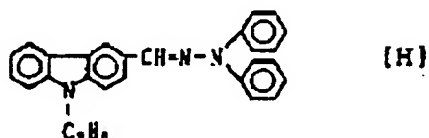
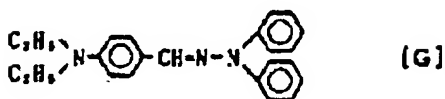
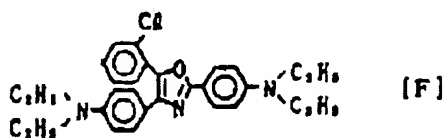
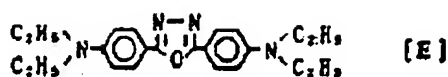
Application Examples 19-21

Photosensitive materials were prepared with the same structure and using the same method as that in Application Example 18, except that instead of styryl compound (3) used in Application Example 18, styryl compounds (20), (33), (38) were used.

For the obtained photosensitive material, the same method as that in Application Example 18 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Comparative Examples 1-4

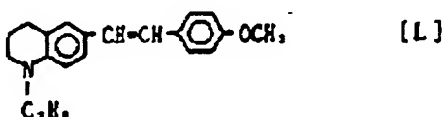
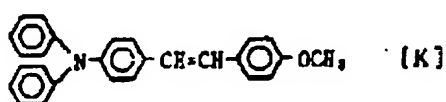
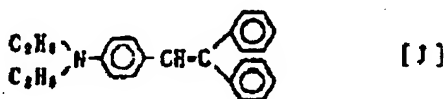
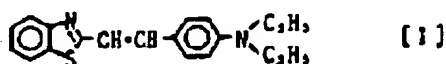
Photosensitive materials were prepared with the same structure and using the same method as that in Application Example 18, except that instead of the styryl compound used in Application Example 18, the following listed compounds (E), (F), (G), (H) were used.



For the obtained photosensitive materials, the same method as that in Application Example 18 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Comparative Examples 5-8

Photosensitive materials were prepared with the same structure and using the same method as that in Application Example 18, except that instead of styryl compound (6) used in Application Example 18, the following listed compounds (I), (J), (K), (L) were used.



For the obtained photosensitive material, the same method as that in Application Example 18 was adopted to determine the values of V_0 , $E_{1/2}$ and DDR_1 .

Table 1 lists the results of measurement of V_0 , $E_{1/2}$ and DDR_1 of the photosensitive materials prepared in Application Examples 1-21 and Comparative Examples 1-8.

As can be seen from Table 1, for the photosensitive materials of the present invention, either the laminated type or single-layer type, the charge holding property is sufficient, the dark

decay rate is sufficiently low for good use as photosensitive material, and the sensitivity is also high as can be seen from the data.

Also, an actual copying test was performed on a commercially available electrophotographic copier (EP-350Z, product of Minolta Camera Co., Ltd.) for the photosensitive material prepared in Application Example 18 by copying 1,000 sheets in the repeated positive charging mode. The gradation was found to be excellent, there was no variation in sensitivity and vivid pictures could be obtained for both the first and last copies. This indicates that the photosensitive material of the present invention also has a high stability in the repetitive operation characteristics.

Table 1

	V_0 (V)	$E_{1/2}$ (lux · sec)	DDR ₁ (%)
① 实施例 1	-660	1.2	2.7
实施例 2	-650	0.8	3.1
实施例 3	-660	0.7	2.8
实施例 4	-660	0.7	2.6
实施例 5	-650	1.0	3.5
实施例 6	-660	0.9	2.8
实施例 7	-650	0.8	3.2
实施例 8	-660	1.0	2.7
实施例 9	-670	1.2	2.3
实施例 10	-660	1.3	2.6
实施例 11	-670	1.0	2.4
实施例 12	-660	1.3	2.6
实施例 13	-670	1.8	2.3
实施例 14	-670	1.5	2.4
实施例 15	-660	0.7	2.7
实施例 16	-650	0.6	3.1

Key: 1 Application Example

Table 1 (continued).

	V_p (V)	$E_{1/2}$ (lux · sec)	DDR ₁ (%)
①	实施例17	- 6 6 0	0 . 8
	实施例18	+ 6 2 0	1 3 . 0
	实施例19	+ 6 1 0	1 3 . 7
	实施例20	+ 6 1 0	1 4 . 1
	实施例21	+ 6 2 0	1 3 . 1
②	比较例1	+ 6 2 0	3 6 . 0
	比较例2	+ 6 0 0	5 . 7
	比较例3	+ 6 0 0	3 . 2
	比较例4	+ 6 1 0	4 . 7
	比较例5	+ 6 2 0	1 5 . 0
	比较例6	+ 6 1 0	5 . 8
	比较例7	+ 6 0 0	6 . 5
	比较例8	+ 6 2 0	8 . 3

Key: 1 Application Example
 2 Comparative Example

Effects of the invention

The present invention provides a type of photoconductive compound that can be used in preparing photosensitive materials.

The styryl compound as the photoconductive composition in the present invention is especially useful as a charge-transporting substance.

The photosensitive material having the styryl compound of the present invention has excellent characteristics, such as sensitivity, charge-transport property, initial surface potential, dark decay rate, etc. Also, it has little optical fatigue in repeated operations.

Brief description of the figures

Figures 1-5 are schematic diagrams illustrating the photosensitive material of the present invention. Figures 1, 4 and 5 illustrate the structure of the dispersion type photosensitive material having a photosensitive layer laminated on an electroconductive substrate. Figures 2 and 3

illustrate the structure of the function-separation type photosensitive material having a charge generation layer and a charge transport layer laminated on an electroconductive substrate.

- 1 Electroconductive substrate
- 2 Charge-transporting substance
- 3 Photoconductive substance
- 4 Photosensitive layer
- 5 Charge transport layer
- 6 Charge generation layer
- 7 Surface protective layer
- 8 Intermediate layer

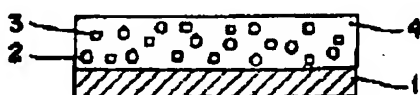


Figure 1

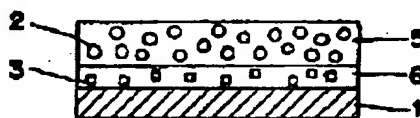


Figure 2

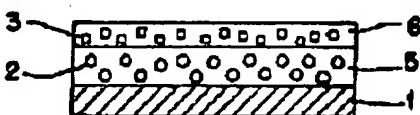


Figure 3

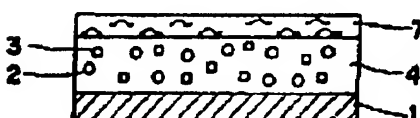


Figure 4

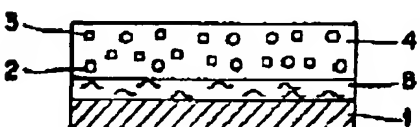


Figure 5

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